Dense Diffusion Barrier Limiting Current Oxygen Sensors

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Abstract

A new type of miniature amperometric oxygen sensor has been developed.   The sensors are high temperature micro-electrochemical devices that use a dense diffusion barrier of a metal oxide that readily transports oxygen and conduct electrons. The diffusion barrier is deposited in thin film form on top of a zirconia-based electrochemical pump. When a voltage is applied to the pump, oxygen is depleted from one side of the diffusion barrier and the ionic current is proportional to the flux of oxygen across the thin film layer. If the pumping voltage reaches a high enough value, the transport of oxygen across the membrane, and hence the device' s output current, will be limited by the external oxygen concentration and the transport characteristics of the diffusion barrier. The sensors can be manufactured in a planar design that offers a faster time response, much simpler design and potentially lower cost than existing limiting current oxygen sensors.

INTRODUCTION

The electrochemical zirconia solid electrolyte oxygen sensor, is extensively used for monitoring oxygen concentrations in various fields.   They are currently utilized in automobiles to monitor the exhaust gas composition and control the air-to-fuel ratio, thus reducing harmful emission components and improving fuel economy. Zirconia oxygen sensors, are divided into two classes of devices: (1) potentiometric or logarithmic air/fuel sensors; and (2) amperometric or linear air/fuel sensors. The potentiometric sensors are ideally suited to monitor the air-to-fuel ratio close to the complete combustion stoichiometry; a value of about 14.8 to 1 parts by volume. This occurs because the oxygen concentration changes by many orders of magnitude as the air /fuel ratio is varied through the stoichiometric value. However, the potentiometric sensor is not very sensitive to changes in oxygen partial pressure away from the stoichiometric point due to the logarithmic dependence of the output voltage signal on the oxygen partial pressure. It is often advantageous to operate gasoline power piston engines with excess combustion air; this improves fuel economy and reduces hydrocarbon emissions. To maintain stable combustion away from stoichiometry, and enable engines to operate in the excess oxygen (lean burn) region several limiting - current amperometric sensors have been reported.[1-6] These sensors operate on the principle of gas diffusion limited electrochemical pumping of oxygen in a platinum electrode-zirconia electrolyte cell. The sensor current plateau is linearly proportional to the concentration of oxygen in the external environment. and the oxygen concentration as shown in Figure 1. This phenomenon occurs because the diffusion of the oxygen through the gas diffusion barrier is the rate-

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determining step.   Two types of physical diffusion barriers are currently being evaluated by the automotive industry : **a**) Figure 2. illustrates a cavity with a small diffusion hole and **b**) Figure 3. illustrates a porous ceramic layer on the cathode to limit the oxygen transfer rate from the ambient gas. They typically show reproducible limiting current plateaus with an applied voltage caused by the gas diffusion overpotential at the cathode.

The aperture type of limiting current sensors requires that the hole does not occlude or change dimensions during long term operation and is relatively expensive to manufacture. The porous diffusion layer is easier to fabricate but controlling the porosity of the layer is a difficult step in the manufacturing process. Long term operation of this sensor may suffer from a drift in the response from a changing pore morphology over time.

The problems associated with pore based diffusion barriers may be overcome, however, by using a mixed electronic and oxygen ion-conducting solid membrane as a diffusion barrier. These materials are known to transport oxygen via motion of lattice site defects which are typically oxygen vacancies. The high electronic conductivity of these materials precludes oxygen ion migration in an electric potential gradient. The motion of the oxygen species is thus only the result of an oxygen chemical potential gradient from the surface to the zirconia interface.   The diffusion of oxygen through the mixed conducting solid materials is much slower than in a gas. This slower diffusion will reduce the oxygen flux to the cathode and, consequently, will linearize the sensor performance.   By applying a thin, or thick,

film of mixed conductor layers, the entire area will be an effective diffusion barrier.[6] As the mixed conductor also exhibits very high electronic conductivity, it will also act as a cathode, and the charge transfer reaction will occur across the entire mixed conductor and solid electrolyte interfacial area.[7] A number of mixed conducting compounds have been identified and used as fuel cell cathode materials. The lanthanum transition metal oxide perovskite structure ceramics represent the largest class of suitable materials. Other suitable compounds include rare earth and transition metal doped ceria and zirconia based fluorite and pyrochlore oxides. These materials are selected for high thermal and chemical stability, and good thermal expansion coefficient match with zirconium oxide. In this document, we report on the fabrication and testing of limiting-current oxygen sensors that utilize mixed conductors as diffusion barriers.

EXPERIMENTAL

 Yttria-doped (3 mole %) tetragonal zirconia (TZ) ceramics and single crystal yttria (8 mole %) stabilized zirconia (YSZ) substrates were used as oxygen ion conducting solid electrolytes. A single 50mm diameter, hot-pressed target of $La_{0.84}Sr_{0.16}MnO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ were purchased from SSC (Seattle Specialty Ceramics) for use as solid oxide mixed conducting diffusion barriers. Lanthanum strontium manganese materials for screen printing were SSC powders, ground and sieved to pass through a 600 mesh screen. Phase purities were confirmed with Bragg Bretano X-ray powder diffraction.

The basic geometric configuration of the limiting-current sensor is shown in Fig. 4. Typical thickness values of the TZ disks and YSZ substrates were about 0.07 cm and 0.05 cm respectively. The mixed conductors were deposited by a 90° off-axis radio-frequency (RF) magnetron sputtering technique. The solid electrolytes were mounted to a quartz lamp heated plate using silver paste, and the substrate heater temperature was measured using an IR camera. All depositions were performed at an RF power of 100 W at a temperature of 700° C. After the depositions, the chamber was flooded with pure oxygen to a pressure of 5 Torr, and the films were allowed to cool. Films from 0.5 to 10 microns in thickness were produced using this technique.

Metal oxide diffusion barrier electrodes were also applied as screen printed thick films (50-150 μm) where glycerol was used as the screen printing vehicle. The thick films were dried at approximately 150°C to remove the vehicle and then fired at 1350°C to densify the electrodes. For electrical testing, platinum contact pads were sputtered to both faces of the devices and thin platinum wires were parallel-gap-welded on both electrodes, as shown in Fig. 4. Electrochemical oxygen leakage from the edges of the devices was reduced by the application of an albite glass seal around the circumference of the sensors. The sensors were placed inside a quartz tube mounted inside the furnace to provide a controlled Ar/O_2 atmosphere and a controlled temperature.

Oxygen and argon gas mixtures of controlled oxygen pressures, ranging from 0.01 to 20% were applied to the sensors. The mixing and the flow rate of the gas were

controlled by a MKS Instruments mass flow controlling system (Model 129A and Model 24C 4-channel readout). All oxygen partial pressures were checked and monitored by an oxygen analyzer (Ametek) connected the exhaust tube of the system. The gas flow rate was approximately 150 cc/min.

The sensor current-voltage characteristics were measured using a Solartron 1286 Electrochemical Interface or an EG&G Princeton Applied Research 273 Potentiostat/Galvanostat and the data was recorded using a digital computer. An oxygen partial pressure was fixed with the gas mixing apparatus and measured using the Ametek oxygen analyzer. Polarization potentials were incremented from 0 - 4 volts and the corresponding electrochemical current was recorded for each device. The furnace temperature was then changed and the measurements were repeated. Figures 5 and 6 illustrate the constant temperature sensor responses. Figures 7, 8 and 9 illustrate the sensor responses at various temperatures.

DISCUSSION

The current-voltage characteristic curve of a typical sensor has four regimes that represent different electroactive processes similar to the response observed in other types of limiting current sensors. [8-11] In the initial region, the current increases nonlinearly with the applied voltage. This increase is believed to be caused by Butler-Volmer type charge transfer kinetics at the mixed conductor / solid electrolyte interface.   The second regime displays an ohmic slope where the output current increases with increasing applied voltage. This behavior is related to the combined ionic transport in the mixed conductor and the solid electrolyte. Taking the slopes as

an indication of the total DC resistivities and subtracting the contribution from the mixed conductors, the DC resistivity of the solid electrolyte can be determined. the mixed conductors have electronic and oxygen ion conductivities that are several orders of magnitude higher than those of the solid electrolyte, the slopes are predominantly caused by the ohmic behavior of the solid electrolyte.

The characteristics of the limiting-current plateau, the third regime, has been studied extensively in devices that use physical diffusion barriers.[1-6] In this region, the rate determining step of our devices is based on the diffusion of oxygen atoms through the lattice of the mixed conductors. Since the electronic conductivity of mixed conductors is high, the internal electric field is very small. Therefore, oxygen transport through these materials occurs only by diffusive motion in a chemical potential gradient and charge transfer occurs at the solid electrolyte-electrode interface.

The sensor current in this third regime can be described using the following relationship:

$$i_l = \frac{4FD_{o_2}SC_{o_2}(0)}{L} \qquad (1)$$

where i_l, F. D_{o_2} S, $C_{o_2}(0)$, and L are the limiting current, the Faraday constant, the oxygen chemical diffusion coefficient through the mixed conductor at the given temperature, the surface area of the mixed conductor (diffusion barrier), the oxygen concentration in ambient gas, and the thickness of the mixed conductor respectively.

Our current - voltage characteristics show that the limiting-current plateaus have a slight slope with increasing applied voltage. The chemical diffusion coefficient of oxygen in the barrier films may be influenced by the very reducing applied polarizations via an oxygen ion vacancy formation mechanism.

Another feature of *i-V* characteristics of the sensors is the observation of a peak at the beginning of the limiting-current plateau. This peak is observed only at the low P_{o_2} current plateaus. Recent unpublished cyclic voltammetry experiments by the authors indicate that the peak is caused by a partial reduction in oxygen stoichiometry of the metal oxide upon application of reducing potentials.

The fourth regime is the current - voltage behavior beyond the limiting-current plateau. This region is expected to be caused by the electrochemical decomposition of the zirconia electrolyte expressed by:[12]

$$O_o^x = V_o^{\cdot\cdot} + \frac{1}{2}O_2(g) + 2e^- \qquad [2]$$
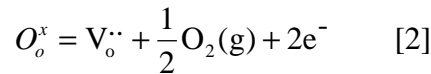
Were O_o^x signifies an oxygen ion on an oxygen site and $V_o^{\cdot\cdot}$ represents an oxygen vacancy. This oxygen loss from the electrolyte exhibits a strong temperature dependence and thus limits the polarization voltages that can be applied at very high operating temperatures.

The dynamic measurement range for these limiting current sensors is determined by a number of device parameters. The highest oxygen concentration detected by our thin film sensors is about 2000 to 3000 ppm. Figures 7, 8, and 9 show that the range

of oxygen concentration detected is larger with higher temperature. As the temperature is lowered, the detection range of the sensor gets narrower due to the higher conductivity of the solid electrolyte with increasing temperature. The ionic conductivity of the solid electrolyte predominately determines the slope in the second regime of the i-V curve. The conductivity of the electrolyte determines the highest possible intercept of the ohmic part in the i-V plot. To increase the range of measureable oxygen concentration, a more conductive or thinner solid electrolyte can be used. The range can be increased significantly by using thin-film solid electrolyte technology .

The oxygen sensor response can be further optimized by tailoring the thickness of the barrier layer for the oxygen concentration range that is desired. The mixed conductors used as diffusion barriers for our oxygen sensor have a relatively high oxygen diffusion coefficient. The high mobility of oxygen through the mixed conductor diffusion barrier limits the sensor' s detection range at the currently used thickness. To increase the operating concentration range the thickness of the diffusion barrier layer can easily be increased with currently available thick film technology such as screen printing. Figures 10 and 11 illustrate the response of such a 50 micron thick film device fabricated by the authors. The device displays excellent response characteristics from 0.5% oxygen concentrations to ambient air oxygen partial pressures. Alternatively dense diffusion barrier materials with a lower diffusion coefficient for oxygen can also be used.

Our sensors based on $La_{0.8}Sr_{0.2}CoO_3$ diffusion barriers, displayed a long term drift in the limiting current plateaus when subjected to polarization voltages of over 2 volts and temperatures of 800°C. Optical examination of the devices revealed significant morphological changes of layers and XRD analysis confirmed phase decomposition.   The $La_{.84}Sr_{.16}MnO_3$ material proved to be a more stable material, exhibited better chemical stability and thus proved to be the diffusion barrier of choice of these perovskites. Lanthanum manganate based sensors have already demonstrated hundreds of hours of continuous laboratory operation.

CONCLUSIONS

We have demonstrated the incorporation of dense oxide based chemical diffusion barriers in solid state limiting current oxygen sensors. Solid oxide fuel cell cathode perovskite materials such as lanthanum strontium cobalt oxide and lanthanum strontium manganese oxide function both as electrodes and dense diffusion barriers. Simple thick film ceramic deposition methods such as screen printing may be used to fabricate these devices as opposed to the micro-machined cavities used in aperture type devices and the plasma or flame sprayed porous coating used in other types of amperometric devices. The simplicity of the planar non-porous design of these sensors may substantially lower the cost of manufacture of wide range oxygen sensors.

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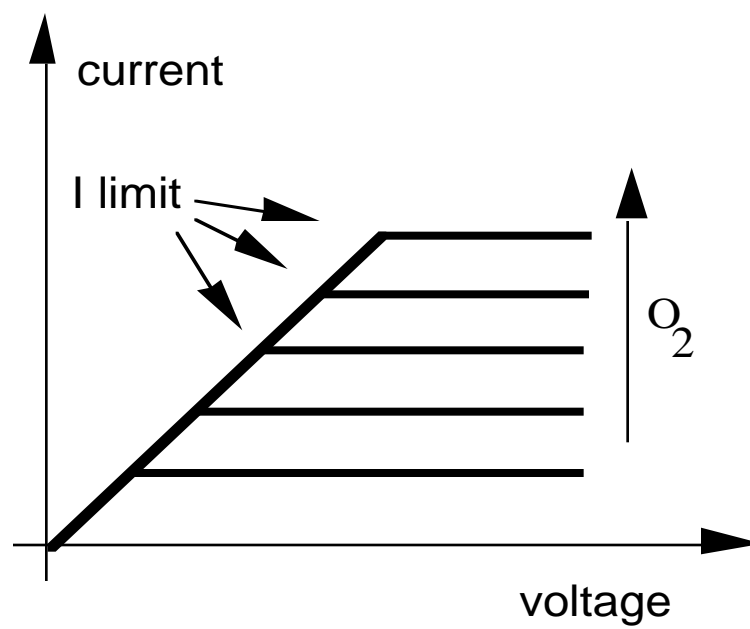
Figure 1. Limiting current oxygen sensor behavior as a function of gas concentration

exhaust gas

aperture

ceramic cap

solid electrolyte

platinum electrode

V

I
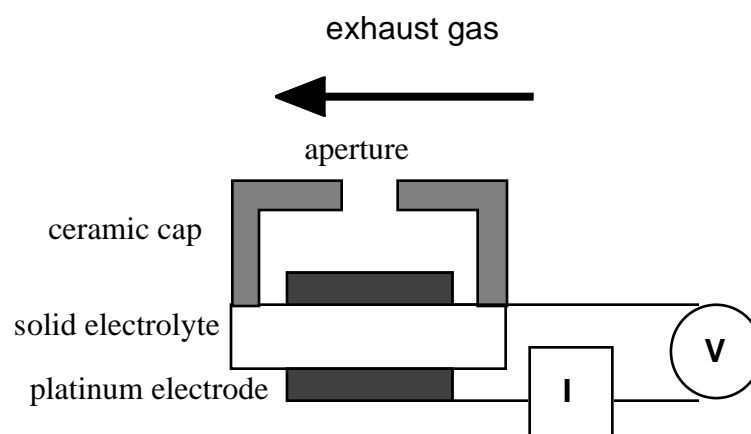
Figure 2. Schematic illustration of a cross-sectional view of an aperture type limiting current sensor
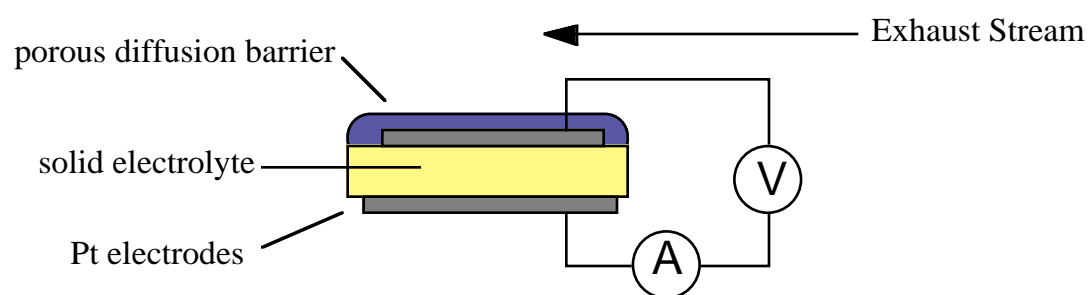
Figure3. Schematic illustration of a cross-sectional view of a porous layer limiting current sensor
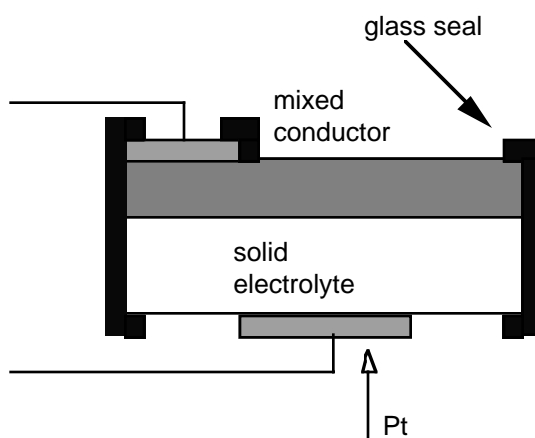
glass seal

mixed
conductor

solid
electrolyte

Pt

Figure 4. Limiting current sensor configuration. A dense mixed conductor oxide film forms the working electrode and a porous Pt film is used for the counter electrode.
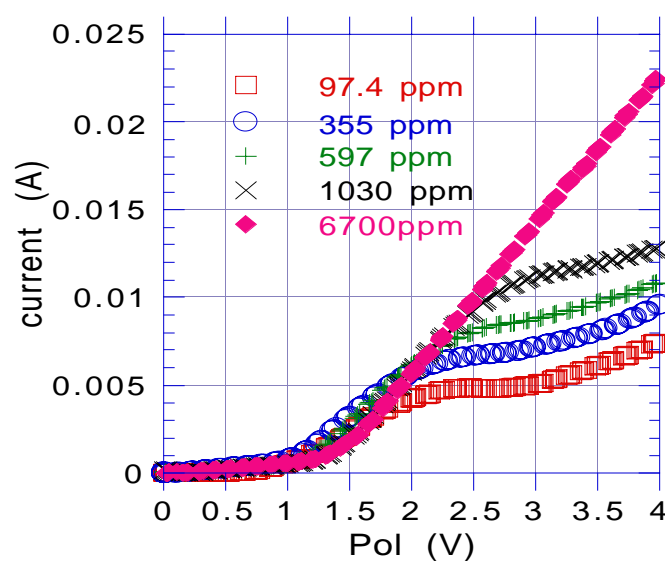
Figure 5. O$_2$ sensor response for a La$_{.84}$Sr$_{.16}$MnO$_3$ film/ yttria stabilized zirconia/platinium device operating at 600 °C
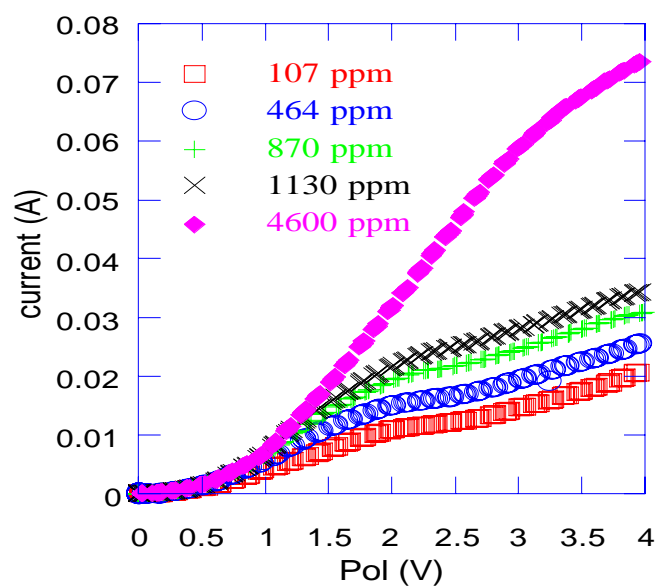
Figure 6 La.$_{84}$Sr.$_{16}$MnO$_3$ /tetragonal zirconia /Pt oxygen sensor reponse at 800 °C
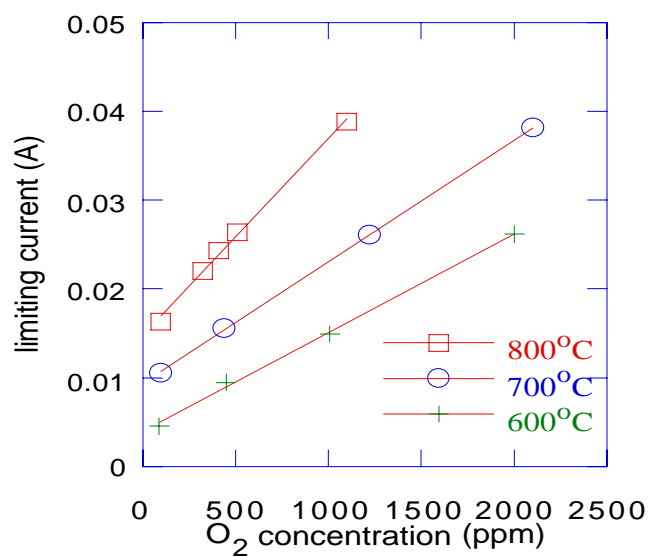
Figure 7. La.$_{84}$Sr.$_{16}$MnO$_3$/ yttria stabilized zirconia/Pt   device response at varying temperatures
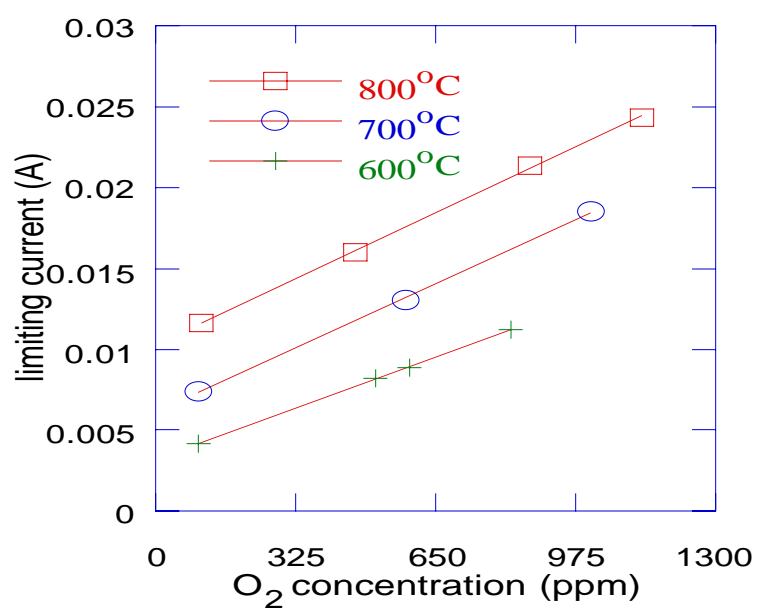
Figure 8. La.$_{84}$Sr.$_{16}$MnO$_3$ thin film /tetragonal zirconia /Pt sensor response as a function of temperature
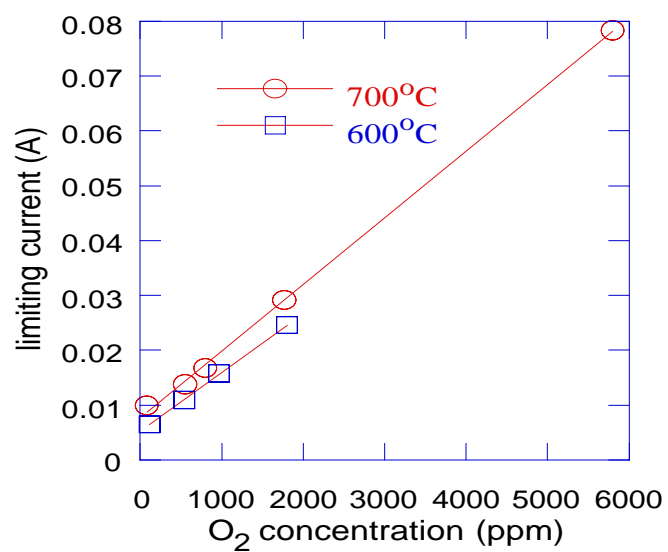
Figure 9. La$_{0.8}$Sr$_{0.2}$CoO$_3$/tetragonal zirconia/Pt sensor oxygen response

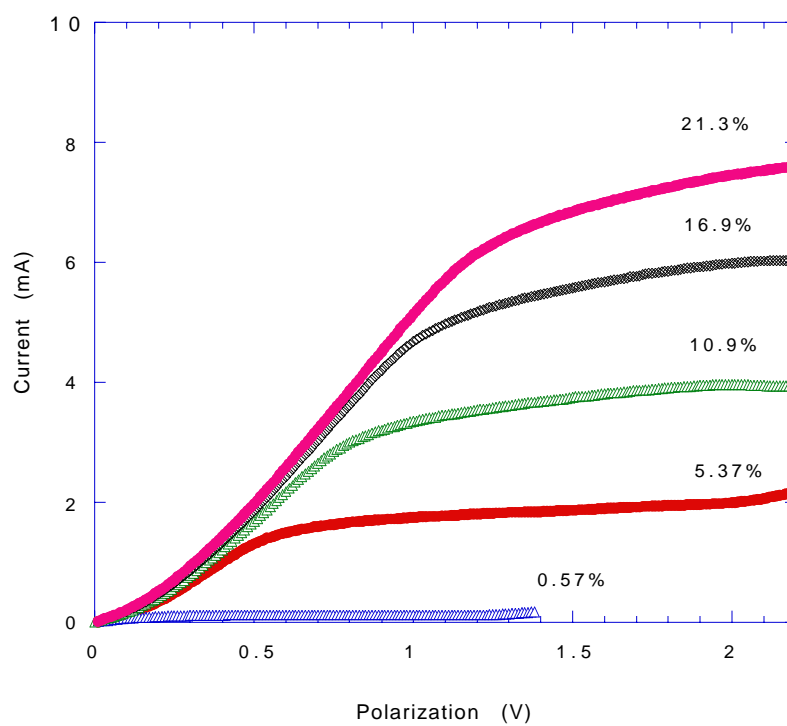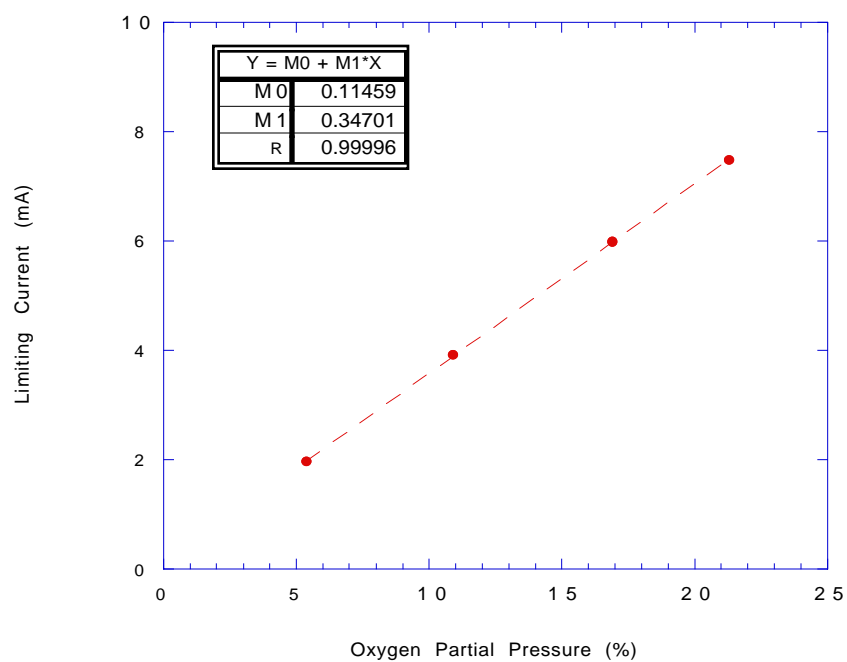*Figure 10. La.$_{84}$Sr.$_{16}$MnO$_3$ thick film - 50 microns /YSZ/ Pt sensor response for varing partial pressures of oxygen . at 700 °C*

Figure 11. Oxygen pressure- current output data for the $La_{.84}Sr_{.16}MnO_3$ thick film - 50 microns /YSZ/ Pt sensor taken at 700°C